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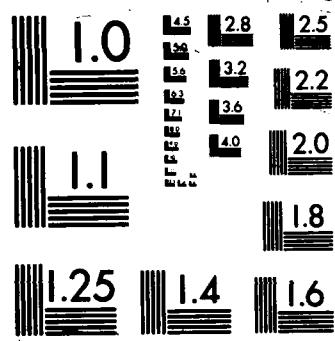
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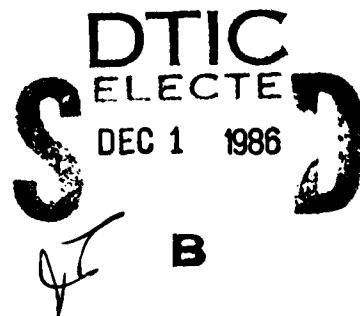
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by

C.V. Berney, P. Cheng, P. Kofinas and R.E. Cohen
Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

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SANS STUDIES OF THE CONFIGURATIONS OF SINGLE CHAINS
IN HETEROGENEOUS BLOCK COPOLYMERS

C.V. BERNEY, P. CHENG, P. KOFINAS AND R.E. COHEN
Massachusetts Institute of Technology
Cambridge, MA 02139

ABSTRACT

Small-angle neutron scattering studies of polystyrene-polybutadiene diblock copolymers of spherical morphology are discussed, with emphasis on the effect of this morphology on the spatial organization of the polymer chains. Three particular cases are examined: (i) the distribution within the matrix of added (matrix) homopolymer, (ii) the distribution within the spherical microdomains of added (microdomain) homopolymer, and (iii) isotopic effects occurring in the B domains when a B-deuterated diblock SB_d is blended with a normal sample SB. Deviations from ideal mixing are found in all three cases.

INTRODUCTION

Heterogeneous block copolymers present well-ordered morphologies which have been the object of numerous experimental and theoretical studies [1-3], including a considerable amount of small-angle neutron scattering work [4]. In our research program on polystyrene-polybutadiene diblock copolymers (SB) with spherical polybutadiene (B) domains, we have examined the spatial arrangement of the spheres [5], the sphere size in relation to B molecular weight [6,7] and the nature of the interfacial zones in these materials [7]. In addition we have successfully exploited the principle of isotopic "contrast matching" [8,9] to obtain information on the configurations of the diblock B chains within the spherical domains [10].

Recently we have been concentrating our efforts in this latter area, namely the spatial organization of chain molecules within the block copolymer morphology. We are particularly interested in this topic because we view the microphase-separated morphologies of block copolymers as a host medium which is perfectly suited for the examination of spatially constrained chains, a

class of problems anticipated some time ago by de Gennes [11]. In this brief survey we report on the results of our work on several of these problems, including: (i) the distribution of matrix homopolymer of various molecular weights in block copolymers of spherical morphology, (ii) the spatial confinement of homopolymers of various molecular weights within the spherical domains and (iii) a reexamination, in light of new theories, of our earlier results [10] on the chain configurations of the portions of the block copolymer which form the spherical domains.

MATERIALS AND METHODS

Except as noted in Table 1, all block copolymers and homopolymers were synthesized in our laboratory using techniques of anionic polymerization described in detail elsewhere [7]. Following extensive molecular characterization, samples of pure diblock or blends of diblock and homopolymer were spin cast [12] into film specimens of about one mm thickness which were then vacuum annealed and laminated [5-7, 10] into specimens of suitable dimensions for small-angle neutron scattering (SANS) experiments.

Table 1: Results of Molecular Chain Characterization

Sample	M_n^S (kg/mole)	M_n^B (kg/mole)	$(M_w/M_n)^{SB}$
SB1	79	11	1.06
SB _d 1	92	13	1.07
SB7	560	59	1.11
SB _d 3	380	46	1.10
B _d 1		9	1.03
B _d 2		19	1.07
S _d 1*	68		1.07
S _d 2*	196		1.12
S _d 3*	385		1.07

*Obtained from Polysciences, Inc., Warrington, PA



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SANS experiments were performed on the 30 meter instrument at the National Center for Small-Angle Scattering Research at the Oak Ridge National Laboratory. These experiments utilized neutrons of wavelength $\lambda = 4.75 \text{ \AA}$ and various sample-to-detector distances. Methods of correcting for background scattering and detector sensitivity have been discussed in our previous papers and will be discussed further elsewhere [13]. The absence of any preferred orientation in the spherical morphology allows us to carry out radial averaging of the symmetric two-dimensional SANS scattering patterns obtained. Complementary electron microscopy has proven valuable in our studies; Phillips 200 and 300 instruments have been used to examine osmium-tetroxide-stained ultramicrotomed sections of the various samples.

RESULTS AND DISCUSSION

Figure 1 presents some of our results which pertain to our examination of perdeuterated homopolystyrene molecules S_d which have been added to the continuous polystyrene matrix of diblock SBl (See Table 1 for molecular characteristics). Although two concentrations of added homopolymer have been examined, 11% and 26%, where the quoted percentage of homopolymer is calculated on a polybutadiene-free basis, only the 11% data are shown here. We have attempted to describe the total scattering from these samples according to the following equation [13].

$$I(Q, R_{hs}, R_o) = I_{chain}(Q, I_o, R_g) + KS(Q, R_{hs})f_{sphere}^2(QR) + I_{inc} \quad (1)$$

where I_{chain} is the scattering from the labeled S chain as calculated from the Debye equation [10,14], K includes the appropriate contrast factor, S is the interference factor for which we have used the Percus-Yevick formalism [15,16], f is the interparticle scattering form factor [5,6,13] and I_{inc} is the incoherent scattering which for these samples was constant at 0.85 cm^{-1} .

Inspection of Fig. 1 shows that in general, the algorithms do a remarkably good job of accounting for the experiment. Two discrepancies, however, are immediately apparent. The first is that the observed interparticle interference peak is broader about the base than the calculated peak. We take this to imply that there are ways in which the arrangement of B domains in the S matrix does not correspond to a hard-sphere distribution, and it

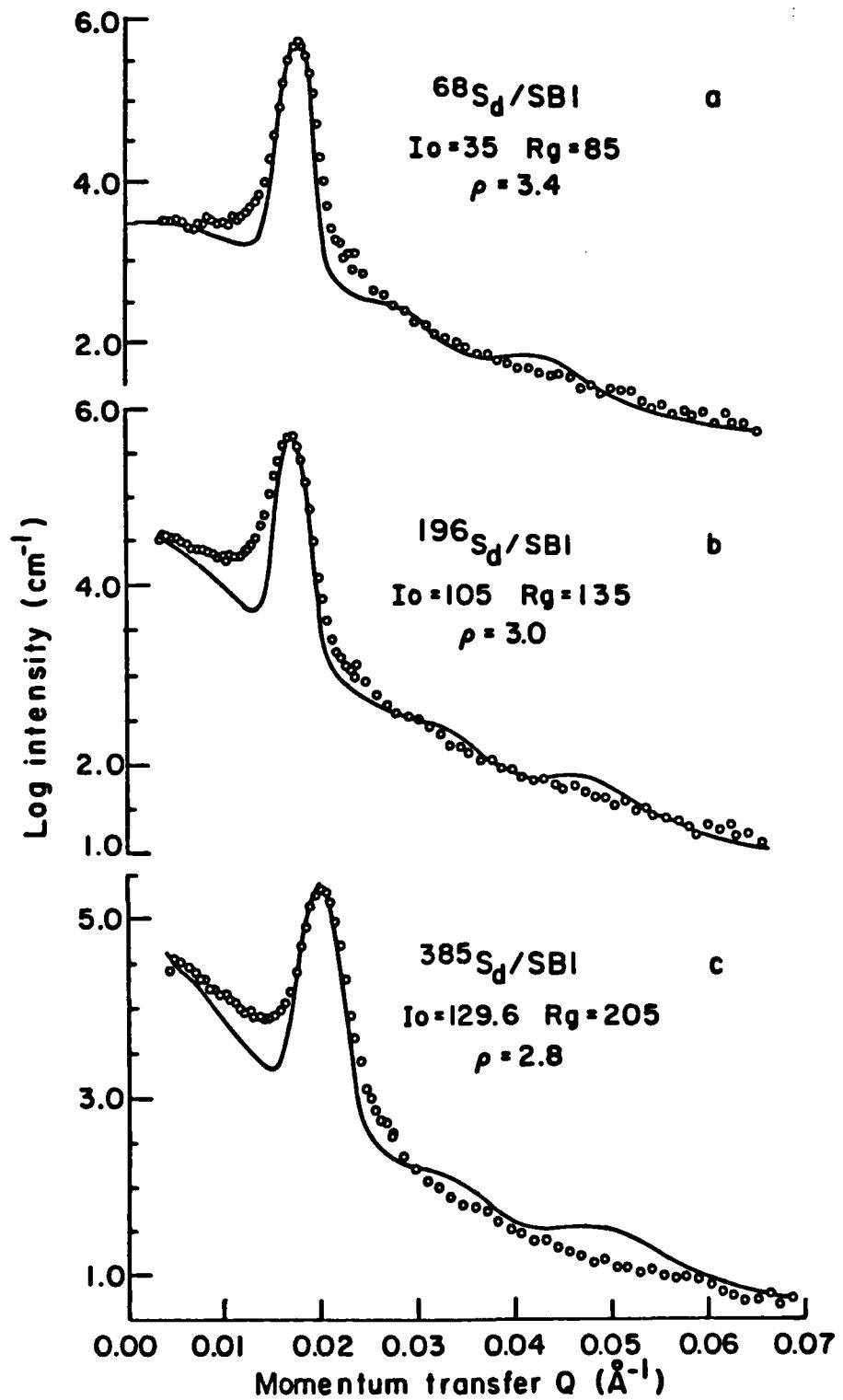


Fig. 1. SANS data for samples containing 11t S_d in SBI (the molecular weight in kg/mole of the blended S_d is indicated by the left superscript). Line indicates scattering calculated from Eq. 1 using parameters indicated on the figure.

may be that the existence of "strings" of spheres, as seen in some of our micrographs, is responsible for this discrepancy. The second discrepancy is the complete absence in the observed spectra of a broad peak around 0.05 \AA^{-1} due to intraparticle scattering from the polybutadiene spheres, present in the calculated spectra and clearly seen in SAXS data [13] not shown here. The meaning of this discrepancy is discussed in detail elsewhere [13]; briefly we note that the intraparticle peak is expected because we implicitly assumed that the S_d chains were distributed more or less uniformly through the polystyrene matrix. The absence of this peak in the SANS data forces us to take seriously the idea of the "hard spheres" used in the Percus-Yevick term described above. As has been pointed out before [17,18], the B domains in an SB diblock-S blend are surrounded by a corona of the diblock S segments attached to the B segments comprising the spherical domains. This corona separates the B domains and determines the effective hard-sphere radius used in the calculations.

Figure 2a shows the neutron scattering-length density ρ for sample SB1 in the vicinity of a B sphere. If the 11% added S_d is assumed to be distributed uniformly through the polystyrene matrix, ρ is raised from 1.414 to 1.97; for 26% added S_d , ρ becomes 2.73 (dashed lines). However, if we assume that the added S_d is excluded from the corona, the interstitial regions are necessarily enriched in S_d . If we take the size of the corona to be the same as the hard-sphere radius determined from the Percus-Yevick model, we can calculate that for the 11% samples ($R_B = 117$, $R_{hs} = 200 \text{ \AA}$), the volume fraction of S_d in the interstices is 0.337, and the corresponding ρ is 3.12 (Fig 2b). For the 26% samples ($R_B = 117$, $R_{hs} = 215 \text{ \AA}$), the interstitial fraction of S_d is 0.705-- the interstices are now mostly deuterated -- and ρ increases to 4.98 (Figure 2).

Consideration of Figure 2 leads to an explanation of the missing intraparticle scattering maxima in the SANS spectra because S-B contrast is now overshadowed by the contrast between the labeled interstitial S_d and coronal regions; a more realistic profile would include some intermixing of the labeled interstitial S_d and unlabeled corona S leading to still further loss of intraparticle scattering intensity. In the SAXS spectra mentioned above, the contrast arises from density differences which are dominated by the difference between glassy S (labeled and unlabeled) and rubbery B;

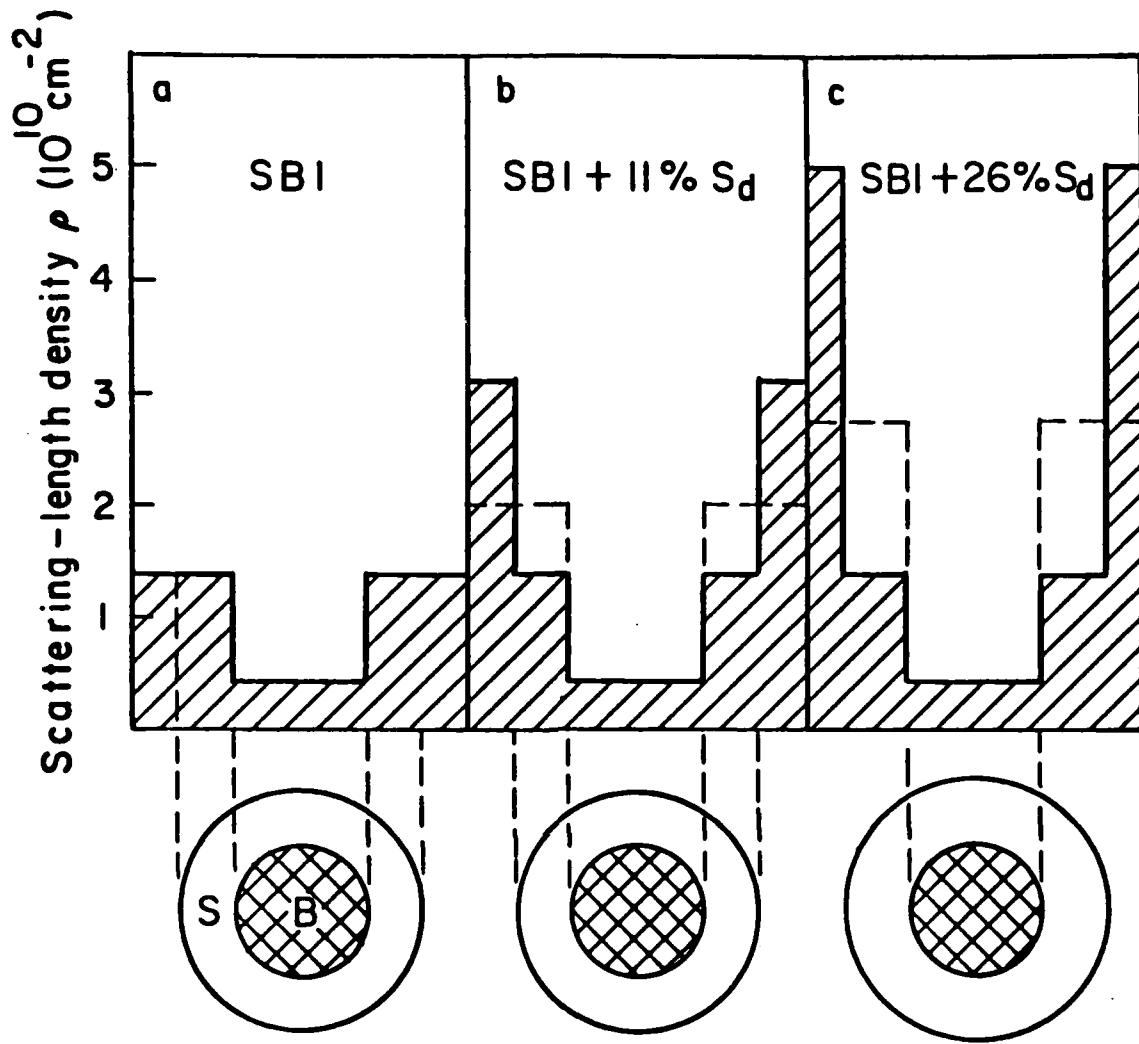


Fig. 2. Scattering-length density profiles for SB systems. Dashed profiles in (b) and (c) indicate calculated ρ if the added S_d is distributed uniformly through the matrix; cross-hatched profiles indicate ρ 's obtained if S_d is assumed to be concentrated in the interstitial regions. SANS observations indicate that the latter assumption is more nearly correct.

therefore the intraparticle scattering peaks associated with the presence of the B spheres appear as expected in the SAXS spectra.

Results pertaining to our examination of B homopolymer chains caged within the microspherical B domains of the block copolymer morphology are shown in Figure 3. In the diblock copolymer the B moieties have a molecular weight of about 10,000 g/mole; perdeuterated B_d homopolymers of about 10,000 g/mole and 20,000 g/mole were blended with the diblock in quantities (16% perdeutero B_d on a S-free basis) which were expected [10] to provide contrast matching with the S matrix. As seen clearly in Figure 3, contrast matching was not achieved in either spectrum; the spectrum for the blend containing the higher molecular-weight (20,000 g/mole) B_d showed exceedingly large deviations from the Debye curve associated with Gaussian B chains of this molecular weight whereas the other blend containing 10,000 g/mole B_d deviated only slightly from the expected single-chain scattering curve. TEM examination of these blends showed clearly that a considerable amount of the 20K B_d was not incorporated into the B domains of the block copolymer; many large B pools of about 1 μm diameter were observed. Thus the large amount of structural scattering for the 20K blend arises from failure to achieve the desired contrast matching, which would have occurred if all the labeled 20K B_d had been distributed uniformly throughout the B domain structure. The observed scattering from the 10K blend is also not well described by the appropriate Debye curve for 10K chains but the deviations are very much smaller than those seen for the 20K blend. TEM revealed only very few pools of 10K B_d ; i.e., contrast matching was essentially achieved for this blend. Therefore one might expect the SANS spectrum of the 10K blend to closely match the spectrum obtained earlier [5] for the SB1 diblock but with all peaks showing much lower intensities owing to the reduced or nearly eliminated contrast factor. However, the 10K blend spectrum is not at all like that of SB1; peak shapes and locations are significantly different. This leads us to speculate that the labeled 10K B_d , although essentially fully incorporated into the domains, may not be uniformly distributed within these domains. This would lead to a multistep scattering density profile, qualitatively similar to those described above in Figure 2, and to a SANS spectrum containing information on both single-chain behavior and the distribution of the labeled B_d within the domains. Further analysis and experiments are underway to examine these ideas in greater detail.

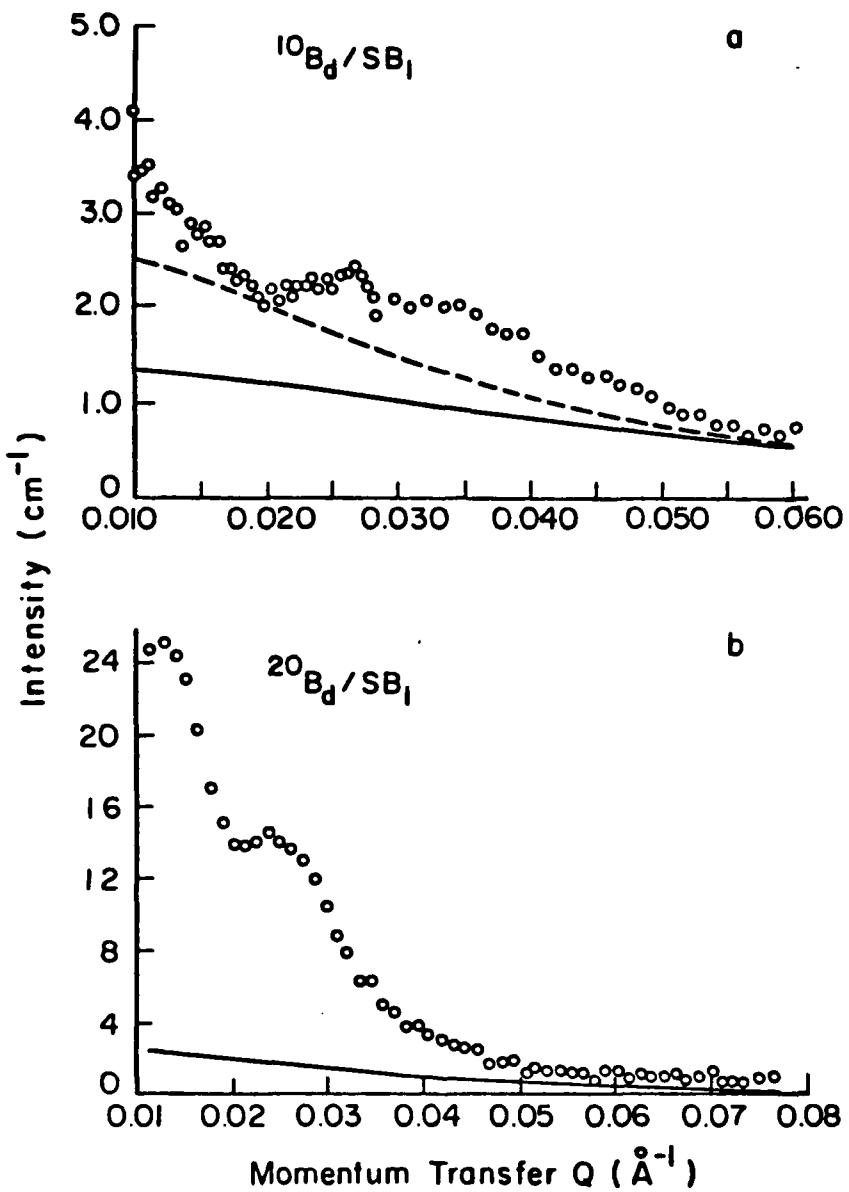


Fig. 3. SANS data for samples containing 16% B_d in SB1 (the molecular weight in kg/mole of the blended B_d is indicated by the left superscript). Deviations from calculated Debye curves (full line) indicate that contrast matching was not achieved.

Finally, we have recently reexamined our earlier analysis of SANS spectra obtained from blends of diblock copolymers SB and SB_d where the appropriate amount of SB_d was chosen to obtain contrast matching. Featureless monotonic SANS spectra were obtained indicating that the contrast matching was successful. The SANS data were used to derive an apparent weight-average polymerization index N_w and a radius of gyration R_g for each of two samples, one of relatively low molecular weight ($SB_d1/SB1$) and one of relatively high molecular weight ($SB_d3/SB7$). The results were compared with values of N_w obtained from more direct techniques (gel permeation chromatography and UV absorption) and values of R_g appropriate for bulk polybutadiene of given N_w . For $SB_d1/SB1$, the SANS value for N_w was found to be within 40 per cent of the GPC/UV value, a result which was taken to indicate substantial agreement. For the higher molecular-weight sample, $SB_d3/SB7$, N_w from the SANS analysis was nearly 4 times that from the conventional characterization. This increase (reflecting an increased level of scattering) was attributed to "clustering" (isotopic phase separation) of the labeled B_d chains within the polybutadiene microdomains.

We had originally concluded [10] that the discrepancy for $SB_d/SB1$ could be explained by uncertainty in our knowledge of the chain length of the polybutadiene block, while the discrepancy for $SB_d3/SB7$ was clearly outside these limits. Since then we have acquired more confidence in the accuracy of our molecular weight measurements (partly due to close agreement between the calculated and observed positions of major structural features in the SANS spectra of unblended SB1 and SB1), and our present feeling is that $SB_d1/SB1$ exhibits extra scattering although clearly less of it than $SB_d3/SB7$ (Figure 4).

De Gennes' formulation [11] of the expected scattering in terms of the Flory parameter x provides a new way of approaching the problem. One can force agreement at low Q by manipulating x rather than N_1 : one finds that the required x for $SB_d1/SB1$ is 0.0043 (5 times the recently reported value [19] for PB/PB_d) and for $SB_d3/SB7$ it is 0.0027 (3 times the reported value). From this point of view, $SB_d1/SB1$ is more anomalous than $SB_d3/SB7$, although in the case of $SB_d1/SB1$, the apparent anomaly is accentuated by the short chain length (the ratio of x^*N_1 for the two samples, where x^* takes on the forced values quoted above, is about the same as the ratio of the discrepancy factors for coherent scattering at low Q quoted above). Thus we now conclude

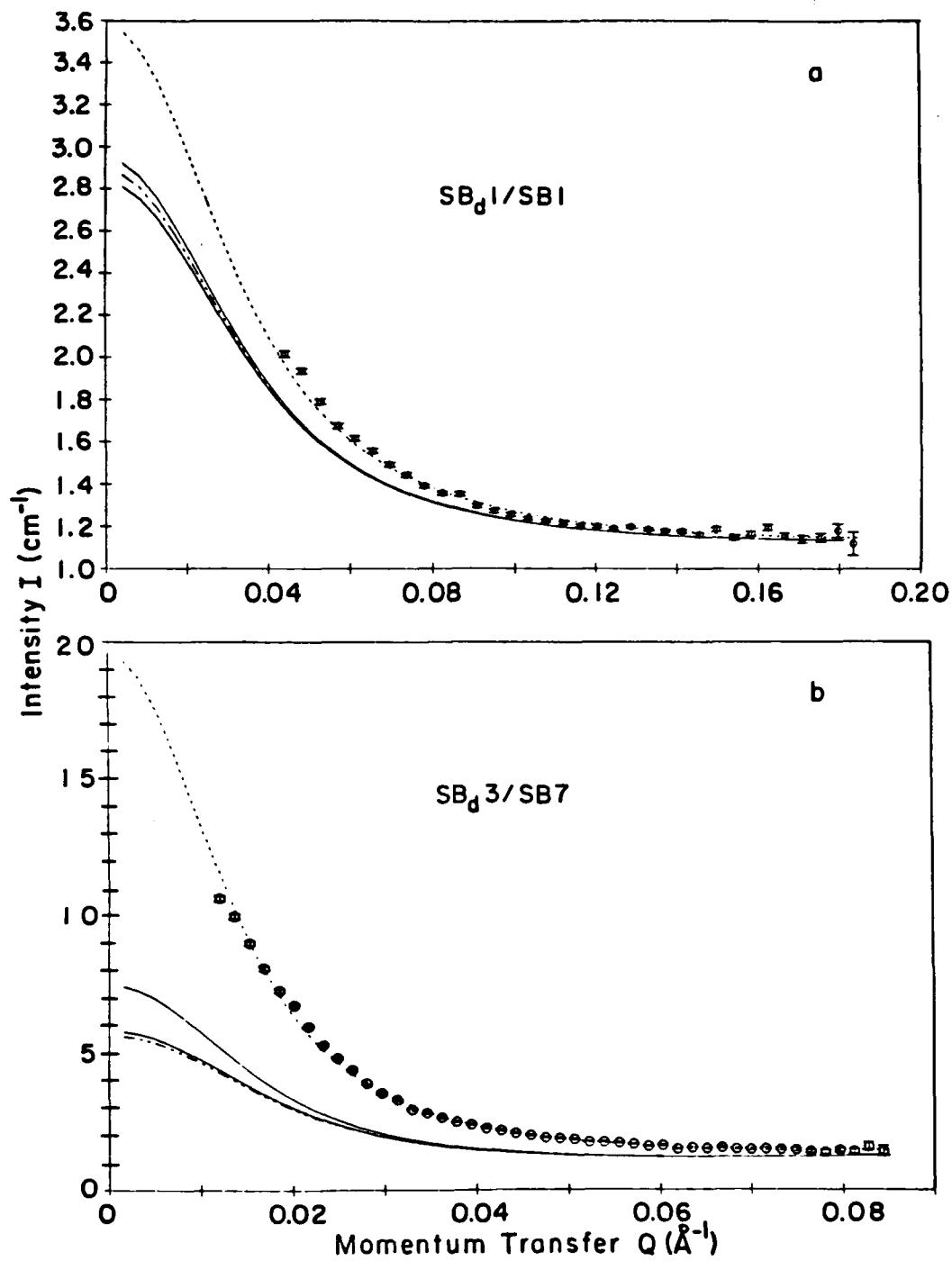


Fig. 4. SANS data for SB_d1/SB1 blends for which contrast matching was achieved. Dashed lines represent Debye curves fit to the scattering data. Dash-dot curves represent Debye calculations using chain parameters (N_w , R_g) derived from GPC/UV characterization of the samples. Full curves represent mean-field calculations based on de Gennes' method[11].

that clustering of labeled chains (or some other chain-length-related mechanism) is operating to produce enhanced neutron scattering in both SB_d1/SB1 and SB_d3/SB7.

SUMMARY

In three separate studies we have observed various deviations from ideal single-chain scattering in block copolymers. In blends of labeled and unlabeled diblocks there appears to be some segregation of the two species, but not to the extent of forming separate labeled and unlabeled domains; contrast matching is essentially achieved in the domains of these blends but it is necessary to postulate some form of segregation within the domains to account for the observed scattering. Consideration of a non-zero χ factor for the labeled and unlabeled chains only partially explains the experimental results. When homopolymer chains are added to the continuous matrix of a specimen of spherical block copolymer morphology, the homopolymer is rejected from the corona and collects in what might be viewed as the interstices between the equivalent hard-sphere regions occupied by the B domains and S corona. Homopolymer chains within spherical domains were also examined; when the homopolymer chain lengths were matched to that of the domain-forming moiety of the diblock, contrast matching was nearly achieved but some pooling of the homopolymer inside the domains was suspected based on SANS and TEM data. For the case of longer homopolymer chains, it was not possible to solubilize sufficient quantities of the labeled homopolymers into the domains to achieve contrast matching; TEM results showed large numbers of micron-sized homopolymer pools forming separately from the block copolymer structure, and therefore the SANS spectrum contained very significant amounts of structural scattering.

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REFERENCES

1. A. Noshay and J.E. McGrath, "Block Copolymers, Overview and Critical Survey", Academic Press, NY 1977.
2. "Developments in Block Copolymers-1", edited by I. Goodman, Applied Science Publishers, London, 1982.
3. J.A. Manson and L.H. Sperling, "Polymer Blends and Composites", Plenum Press, New York, 1976.
4. R.W. Richards, *Adv. Polymer Sci.*, 71, 1(1985).
5. F.S. Bates, R.E. Cohen and C.V. Berney, *Macromolecules*, 15, 589 (1982).
6. F.S. Bates, C.V. Berney and R.E. Cohen, *Macromolecules*, 16, 1101 (1983).
7. C.V. Berney, R.E. Cohen, and F.S. Bates, *Polymer*, 23, 1222 (1982).
8. S.N. Jahshan and G.C. Summerfield, *J. Polymer Sci., Phys.*, 18, 1859 (1980).
9. J.T. Koberstein, *J. Polymer Sci., Phys.*, 20, 593 (1982).
10. F.S. Bates, C.V. Berney, R.E. Cohen and G.D. Wignall, *Polymer*, 24, 519 (1983).
11. P-G. de Gennes, "Scaling Concepts in Polymer Physics" Cornell University Press, Ithaca 1979.
12. F.S. Bates, R.E. Cohen and A.S. Argon, *Macromolecules*, 16, 1108 (1983).
13. C.V. Berney, P. Cheng and R.E. Cohen, to be submitted.
14. P. Debye, *Phys. Colloid Chem.*, 51, 18 (1947).
15. J.K. Percus and G.J. Yevick, *Phys. Rev.*, 110, 1 (1958).
16. D.J. Kinning and E.L. Thomas, *Macromolecules*, 17, 1712 (1984).
17. L.Leibler and P.A. Pincus, *Macromolecules*, 17, 2922 (1984).
18. M.D. Whitmore and J. Noolandi, *Macromolecules*, 18, 657 (1985).
19. F.S. Bates, G.D. Wignall and W.C. Koehler, *Phys. Rev. Letters*, 55, 2425 (1985).

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